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INORGANIC ANALYSIS PROTOCOL
Turbidimetric Analysis of Sulfate and Sulfur

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REVISION NUMBER: 01

1.0 PURPOSE

To determine the sulfate concentration in drinking, surface, and ground waters; and solid matrices (includes modifications for soil preparation).

2.0 REFERENCE

This SOP was written using the following references:

2.1 EPA 600/04-79-020, Method 375.4.

2.2 SW-846, 3rd Ed., November 1986, Method 9038 as a secondary reference. (There are no appreciable differences between the two methods.)

2.3 Standard Methods, 17th Ed., Method 4500-SO₄²⁻ is also a turbidimetric method, but uses significantly different buffers and timing. The timing from this method has been incorporated into this SOP.

2.4 ASTM Method D-129, is used as the reference for sulfur analysis. The analysis of the bomb washings is by EPA Method 375.4.

3.0 METHOD SUMMARY

The turbidimetric sulfate test is used to determine the amount of sulfate ion converted to a barium sulfate suspension under controlled conditions. Sulfate



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ion is precipitated in a Hydrochloric Acid medium with Barium Chloride so as to form barium sulfate crystals of uniform size. The resulting turbidity is determined by a spectrophotometer and compared to a curve prepared from standard sulfate solution.

4.0 INTERFERENCES

4.1 Suspended matter, color, and turbidity are positive interferences that may be corrected for by routinely running color blanks on all samples prior to the addition of barium chloride. Some samples will require pre-filtering as well.

4.2 Silica in concentrations of > 500 mg/L will interfere.

5.0 SAMPLE CONTAINER, PRESERVATION AND HANDLING

Sample container, preservation techniques and hold times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

<u>Regulation</u>	<u>Holding Time</u>	<u>Reference</u>
CWA	28 days	CFR 40 Part 136.3
SDWA	28 days	EPA-570/9-82-002

6.0 INSTRUMENTATION AND EQUIPMENT

6.1 Spectrophotometer

Wavelength of 420 nm and a light path of 1 cm

6.2 Miscellaneous

- an electric timer or a clock with a second hand
- measuring spoon, capacity 0.2 to 0.3 mL
- magnetic stir plate used at a constant speed
- stir bars of identical shape and size
- stir bar retriever

- 250 mL beakers
- 5 mL dispenser containing conditioning reagent
- 100 mL volumetric flasks (standard preparations)
- pipettes, eppendorfs and serological
- small test tubes

7.0 PREVENTIVE MAINTENANCE

- 7.1 The cuvette and spectrophotometer cell must be kept clean. The cuvette must be rinsed with DI prior to analysis. The spectrophotometer cell should be visually examined for any sample spillage or build-up of barium sulfate.
- 7.2 Spectrophotometer must be kept clean at all times. Yearly professional maintenance must be done. Manufacturers recommended calibration procedures must be followed.

NOTE: Do not use the sipper attachments on the spectrophotometer. The Barium Chloride may build up in the flow-through cell.

8.0 STANDARDS AND QC SOLUTIONS

All reagents are prepared with Type II DI Water, unless otherwise stated, in Class A volumetric flasks.

8.1 Conditioning Reagent

In a 2000 mL beaker, add 1200 mL DI Water, 120 mL concentration hydrochloric acid, and 400 mL 95% ethanol or isopropanol making sure the graduated cylinder is rinsed thoroughly after each measurement. Weigh out 300 g of sodium chloride on a top loading balance and add to the above mixture. Add 200 mL of glycerol, a clean stir bar, and place the mixture on a stir plate until all of the sodium chloride dissolves. Transfer the solution to a clean labeled bottle.

- Life of Reagent: one year
- Storage Requirements: store at room temperature

8.2 Calcium Chloride Leaching Solution, 0.15%

To a 1.0 L volumetric flask partially filled with DI water, add 1.5 g calcium chloride (oven dried in a 105°C oven) and fill. Add a clean stir bar and place on a stir plate until all of the calcium chloride is dissolved. Transfer the solution to a clean labeled bottle.

- Life of Reagent: one year
- Storage Requirements: room temperature

8.3 Stock Solution I, 1000 mg SO₄/L

Dry about 3 g of anhydrous Sodium Sulfate (Na₂SO₄) in the oven at 105°C for at least 2 hours. Cool in a desiccator to room temperature. Using an analytical balance capable of measuring 0.1 mg, weigh out 1.4786 g of the dried crystals and add it to a 1.0 L volumetric flask. Dissolve in DI water and dilute to volume. Transfer the solution to a clean and properly labeled bottle.

- Life of Reagent: one year
- Storage Requirements: store at room temperature

8.4 Stock Solution II, 4000 mg SO₄/L

Dry approximately 7 g of anhydrous Sodium Sulfate, from a different manufacturer than Rgt. 8.3, in a 105°C oven for at least two hours. Cool in a desiccator to room temperature. Using an analytical balance capable of measuring 0.1 mg, weigh out 5.9144 g of dried crystals and place in a 1.0 L volumetric flask, dissolve in DI water and dilute to volume. Transfer the solution to a clean and properly labeled bottle.

- Life of Reagent: one year
- Storage Requirements: room temperature

8.5 Barium Chloride Crystals, 20 to 30 mesh

Purchased from a chemical vendor.

- Life of Reagent: three years or manufacturer's recommendation
- Storage Requirements: room temperature



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9.0 PROCEDURE

All sulfate analysis is done on non-preserved (general) samples.

9.1 Reporting Limits

Waters.....5 mg/L
Soils/Wastes.....50 mg/kg

9.2 Sample Size

Waters.....100 mLs
Soils/Wastes.....10 grams

9.3 Sample Preparation

9.3.1 Preliminary Testing

To pre-test, place 8-10 mL of sample in a small test tube with a small scoop of barium chloride and a few drops of conditioning reagent. Shake well and visually compare the resulting turbidity to that of a similarly treated high standard.

9.3.2 Soil/Waste Preparation

9.3.2.1 Weigh out 10 g of sample, to the nearest 0.1 g, in a 250 mL beaker.

9.3.2.2 Add 100 mLs of 0.15% Calcium Chloride Leach Solution to the beaker.

9.3.2.3 Stir the mixture on a stir plate for 60 minutes.

NOTE: Alternatively, weigh the sample into a 250 mL plastic sample bottle, add 100 mL of water and shake for 30 minutes on the wrist-action shaker.

9.3.2.4 Filter the mixture through a Whatman 541 or GF/C filter.

9.3.2.5 Pre-test the filtrate as stated in Section 9.3.1.



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- 9.3.3 Sulfur analysis is done by sulfate analysis of the washings from the firing of a portion of a sample in a Parr oxygen bomb. Pre-test as in Section 9.3.1 and treat the bomb washings as a water sample until calculating the % sulfur result.
- 9.4 Analysis
- 9.4.1 Allow 30 minutes for the spectrophotometer to warm up at 420 nm wavelength. Zero the instrument with DI water.
- 9.4.2 Place 100 mL of standards, blanks, and prepared samples in properly labeled 250 mL beakers. Record the RFW#'s, weight, dilutions, etc., in the date book.
- 9.4.3 To calibrate, first add 5.0 mL of conditioning reagent (Rgt. 8.1) to the blank and each standard of the curve and to the ICV and ICB only. These must be read and in control before color blanks or sample absorbances can be read.
- 9.4.4 Stir each standard or sample for exactly 1.0 minute at constant speed. Set aside the sample and continue with the next standard or blank.
- 9.4.5 Six minutes after the addition of the BaCl_2 to the first beaker, begin reading the standards on the spectrophotometer (wavelength 420 nm). Timing is important. Each sample must be stirred for 1 minute with the BaCl_2 and then allowed to sit for 5 additional minutes prior to reading. Practice will allow a continuous cycle of stirring and reading so that a set of samples may be read efficiently.
- 9.4.6 Stop reading after the curve, ICV and ICB are read. Calculate the correlation coefficient of the curve and the ICV/ICB to insure that they are within control limits (See Section 9.5).
- 9.4.7 Add 5.0 mL of conditioning reagent to each sample aliquot and the QC beakers.

- 9.4.8 Read each sample or sample dilution on the spectrophotometer **without adding Barium Chloride** to correct for color or turbidity that filtering may not have removed. CCVs and CCBs with Barium Chloride must be stirred for 1.0 minute and read after 5 minutes between every ten readings. See Analytical Sequence (Section 9.5).

NOTE: All positive color blank absorbances are subtracted from the sample absorbances prior to the mg/L calculation. Negative color blanks are not subtracted. If a color blank absorbance is higher than the sample absorbance, a note must be made in the data book. If the color blank of an undiluted or lesser diluted sample is zero or negative, a color blank is not needed on a greater dilution of the same sample.

- 9.4.9 Once all of the color blanks are read, beginning reading each sample as described in Sections 9.4.3 - 9.4.5.

9.5 Analytical Sequence

Calibration Controls	Sequence	Control Limit
Standards	prior to samples	y-int < MDL abs.
Corr. Coeff.	prior to samples	≥ 0.995
Init. Cal. Ver. (ICV)	after calibration	90 - 110% Recovery
Init. Cal. Blk. (ICB)	after ICV	< MDL
Cont. Cal. Ver. (CCV)	every 10 readings	90 - 110% Recovery
Cont. Cal. Blk. (CCB)	after every CCV	< Reporting Limit

Quality Controls	Frequency	Control Limit
Prep Blank (PB)	1 in 20 samples	< Reporting Limit
Lab Control Std. (LCS)	1 in 20 samples	+/- 20% Recovery
Lab Control Std. Dup. (LCSD)	1 in 20 samples	$\leq 20\%$ Recovery
Matrix Spike (MS)	1 in 20 samples	+/- 25% Recovery
Matrix Spike Dup. (MSD)	1 in 20 samples	$\leq 20\%$ RPD

All acronyms are defined in Section 12 of this procedure.

Drinking water samples must be done in sets of 10 or fewer samples. The control limits for drinking waters are 90 - 110% recovery for LCSs; RPDs of $\leq 10\%$; and matrix spike recoveries must be 85 - 115% recovery.



9.6 Calibration Procedure

Before any instrument is used as a measurement device, the instrumental response to known reference materials must be determined. The manner in which various instruments are calibrated is dependent upon the particular type of instrument and its intended use. All sample measurements are made within the calibrated range of the instrument. Preparation of all reference materials used for the calibration will be documented.

9.6.1 Instrument calibration consists of the two types: Initial Calibration and Continuing Calibration

9.6.1.1 Initial Calibration

Establishes the calibration range of the instrument and determines the instruments response over that range.

9.6.1.2 Continuing Calibration

Used within an analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that the instrument response did not drift during a period of non-use of the instrument.

9.6.2 Standards Preparation

Standards	Volume of Standard I (Use Eppendorf and/or volumetric pipettes)
0.0 mg/L	100 mL DI Water
5.0 mg/l	500 uL diluted to 100 mL in a vol. flask
7.5 mg/L	750 uL diluted to 100 mL in a vol. flask
10.0 mg/L	1000 uL diluted to 100 mL in a vol. flask
15.0 mg/L	1500 uL diluted to 100 mL in a vol. flask
20.0 mg/L	2000 uL diluted to 100 mL in a vol. flask
25.0 mg/L	2500 uL diluted to 100 mL in a vol. flask
30.0 mg/L	3000 uL diluted to 100 mL in a vol. flask
40.0 mg/L	4000 uL diluted to 100 mL in a vol. flask

Class A Volumetric Flasks are used to prepare the above standards.



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9.6.3 Quality Control Preparation

Quality Control Standard	Volume of Standard II (Use Eppendorf and/or volumetric pipettes)
Init. and Cont. Cal. Blank (ICB/CCB)	100 mL DI Water
Init. and Cont. Cal. Ver. (ICV/CCV), 20 mg/L	500 uL diluted to 100 mL in a vol. flask
LCS/LCSD, 20 mg/L	500 uL diluted to 100 mL in a vol. flask
Matrix Spike, 20 mg/L undiluted sample	500 uL diluted to 100 mL in a vol. flask

10.0 CALCULATIONS

10.1 Water samples

$$\text{mg/L SO}_4 = \text{mg/L (curve)} \times \text{dilution}$$

$$10.2 \quad \text{mg/kg as received} = \frac{\text{mg/L (curve)} \times \text{dilution} \times \text{final volume}}{\text{sample size (g)}}$$

$$10.3 \quad \text{mg/kg dry weight} = \frac{\text{mg/kg as received}}{\% \text{ solids as decimal}}$$

10.4 % Sulfur

$$\text{mg/kg as SO}_4 = \frac{\text{mg/L (curve)} \times \text{dilution} \times \text{volume from bomb}}{\text{bombed sample size (g)}}$$

$$\% \text{ Sulfur} = \frac{\text{mg/kg}}{30,000}$$

10.5 Accuracy

10.5.1 ICV/CCV, LCS/LCSD % Recoveries:

$$\% R = \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$



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10.5.2 Matrix Spike % Recovery

$$\% R = \frac{(\text{spiked sample}) - (\text{unspiked sample})}{\text{spiked concentration}} \times 100$$

10.6 Precision

Matrix Dup. and LCS Dup. Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

10.7 Reporting Results

Without rounding, enter the raw data on the appropriate Lotus spreadsheet. Carefully print, review and approve the spreadsheet. Have the data book and spreadsheet approved and signed by the designated reviewer before creating a print file and transferring the data to LIMS.

11.0 QUALITY CONTROL

11.1 One method blank and two Lab Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

11.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

11.3 The LCS's will be examined to determine both precision and accuracy.

11.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

11.5 Precision will be measured by the reproducibility of both LCS's and will be calculated as relative percent difference (%RPD). Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.



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- 11.6 One matrix spike and matrix duplicate is performed per matrix per 20 sample analytical set. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

12.0 CORRECTIVE ACTIONS

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

- 12.1 Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control has been achieved; and
- receive approval (signature) of the Section Manager, Unit Leader, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

- 12.2 Suggested Actions to specific out of control situations:

12.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.



12.2.2 Initial Calibration Verification (ICV)

- repeat ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- restandardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary;
- prepare new stock and/or working standards and recalibrate;

12.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

12.2.4 Laboratory Control Standards (LCS)

If either LCS1 or LCS2 exceeds acceptance limits:

- reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.)

Precision: LCS1 and LCS2 must meet the control limits of $\leq 20\%$ RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your Section Manager or Unit Leader for proper corrective action.

12.2.5 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level $>$ Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is < 10 times the PB level must be reprocessed and reanalyzed; any sample which is > 10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.



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12.2.6 Matrix Duplicate (DUP)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the \pm Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, a CAR must be written and then approved by your Section Manager or Unit Leader.

12.2.7 Matrix Spike (MS)

- the sample must then be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- the original spike results must be entered onto the spreadsheet with the "S" code even though the control limits were exceeded;
- the reanalysis result must be entered onto the spreadsheet using the "T" code regardless of whether it is within the control limits. There is no need to write a corrective action if both the "S" and "T" codes were entered into LIMS.

12.2.8 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.

12.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;



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- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources).
- never dispose of any samples until you are sure that all QC are within their designated control limits.

13.0 **HEALTH AND SAFETY**

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDSs for the hazardous properties of any chemical or reagent involved in the procedure.



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- Additions to Section 6.0 and Clarification of Section 9.0.